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The Effect of Gases on the Contact Potentials of Evaporated Metal Films

by

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Introduction

When two unlike metals are brought into contact, an exchange of electrons occurs, and the metal with the highest work function becomes negatively charged with respect to the other because of its greater affinity for electrons. The resulting potential difference is called the contact potential or volta potential. The work to move an electron from one metal to the other is the difference of the work functions of the metals. If these are expressed in electron volts, then the difference of the two values is the same as the contact potential difference in volts, as required by the definition of the electron volt. A correction on the order of 0.01 v., ordinarily neglected, is needed because of the difference in density of electrons in the Fermi levels of two metals at a given temperature (Peltier effect).

The work functions of metals have been found to be anisotropic (1, 2, 3), and to vary with allotropic modifications (4, 5). Adsorbed gas films change the effective work function (6) as do oxide films (7). Hence, contact potentials can be used to follow adsorption and reaction with a gas if the metal surface is initially bare.

A very striking effect of gas films was found by Langmuir in his studies on tungsten filaments (8). Emission of electrons from a clean filament was 10^5 times as great as that of a filament covered with a monolayer of oxygen at 1500° K. The work function of clean tungsten is 4.54 e.v.; for tungsten covered with a monolayer of oxygen it is 9.23. On the other hand, a monolayer of barium on the tungsten lowered the work function to 1.56 e.v. (9). Such phenomena may be explained by the relative electronegativities of the metal and the adsorbed atoms. For example, oxygen is strongly electronegative and acquires electrons from the metal to form negative ions. This produces a negative space charge at the surface of the metal, which repels the free electrons in the metal and in effect raises the work function. Barium, being relatively electropositive, donates its valence electrons to the metal and becomes positively charged. The positive space charge at the surface lowers the exit barrier for electrons and decreases the effective work function.

One of the main problems in measuring contact potentials or intrinsic work functions is that of obtaining a pure surface. This difficulty is reflected in the variety of values quoted for the work functions of metals by different workers (10). Various methods have been used to obtain

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a fresh surface, e.g., by cleavage of a metal crystal, by abrasion, by heating - all of these in vacuum (11, 12, 13). Positive ion bombardments have also been used (14). A noble metal with an aged surface is used as a reference, so that contact potential changes between the fresh surface and the reference show the change in work function of the new surface as it oxidizes (15, 16).

A clean surface should be obtainable by preparing evaporated metal films. The properties and uses of evaporated metal films have been recently reviewed by Allen (17). One problem is that of correlating the properties of thin metal films with those of bulk metals. It has been shown by the electron microscope that evaporated films start forming from the vapor as islands or clusters of metal (18), and as a result the electrical resistance of very thin films behave anomalously. Thin films condensed on a cold substrate show negative temperature coefficients of resistance, while thicker films, or films annealed at room temperature, generally have positive temperature coefficients. Films less than 100 Å thick are apt to be affected by the substrate, while thicker ones are not. Films below 100 Å thick may have anomalous properties, while those several thousand Å thick have properties of bulk metals.

Contact potentials are not limited to metal systems. Semi-conductors have definite work functions also, and adsorption on semi-conductors has been observed by contact potential measurements. Yoneda measured potential changes due to the adsorption of water vapor, ammonia, and carbon dioxide on silica gel, the oxides of chromium, iron, aluminum, lead, magnesium and calcium; these materials were pressed into cakes so that a flat surface would be available. The same gases were also used on glass and graphite (19).

The electron beam method as used by Anderson is considered one of the most exact methods for obtaining intrinsic work functions of metals (14, 32). However, the chemist is often interested in measuring the effects of various gases on a metal surface. The vibrating condenser method for observing contact potentials is useful for this type of work.

In this work evaporated films of aluminum, iron, chromium, nickel, and lead were studied by the vibrating condenser method (20), using aged platinum as the reference metal. The potential between the films and the reference were measured in a vacuum system at room temperature as a function of time after evaporation of the film. The potential changes were thus a measure of the change of work function of the evaporated film. The system was so designed that samples of oxygen, nitrogen, and water vapor could be admitted and pumped out at will. This made it possible to distinguish between reversible and irreversible processes of adsorption.

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Successive gas samples were admitted to the system at the same pressure with metering stopcocks. Any required number of samples could be admitted and withdrawn by using the metering stopcocks and a mercury U-seal. This system provided a way to study the reversibility of adsorption and contact potentials.

The Contact Potential Apparatus.

The contact potential apparatus is shown in Fig. 1. The three necks of the flask were sealed with metal fittings, soft soldered. The metal ends of the glass-to-metal seals were soldered to brass adapters as shown. The joints were first cleaned and soldered together without flux, to avoid getting flux inside the vacuum system. The external soldered surfaces were then coated with flux and heated to the fusion point of the solder to insure a tight bond between the surfaces; the structure of the joints were such that no flux could get through the joint during this process.

The evaporating assembly was composed of two 5 mm. brass rods, soft-soldered in 6 mm. glass-to-metal seals. These rods had set-screws in both ends for attachment of tungsten filament in one end and the external power-supply to the other. One of the rods was drilled through to permit attachment of a tungsten wire to support the 18 mm. glass focusing tube. A focusing tube protected the platinum reference from the metal vapor during evaporations. The tube directed the vapor down onto the microscope slide-cover, which was clamped on a cross-bar by a brass spring-clamp. The upper cross-bar was grooved to fit over the lower one; thus the two cross-bars, each loaded with two microscope slide-covers, were installed one at a time through the center neck of the flask. The center neck was sealed with a soft-soldered solid brass cap. The cross-bars were of aluminum, and the lower one contained a strip of soft iron in the lower side to permit moving it from outside with a magnet.

The microscope slide-covers had to be coated on one edge with evaporated metal before use to provide satisfactory electrical contact between the evaporated film and the brass clip on the slide-cover. The soft-glass covers were coated about 3 mm. on one edge with evaporated aluminum, then cleaned and dried prior to use; the brass clip overlapped the area of evaporated metal.

The work of Caldwell (24) and of Olsen, Smith, and Crittendon (25) were useful guides for evaporating methods. Iron and nickel were used in the form of fine wire which was wrapped tightly around the 0.02 inch tungsten filament. Aluminum was evaporated from conical baskets of tungsten wire. Since lead does not wet tungsten well, it was evaporated from nickel wire baskets. Chromium was electrodeposited on the tungsten filament. The evaporated films were checked spectroscopically for tungsten, nickel, and other impurities. These findings are given in Table 1, along with data on the gases used.

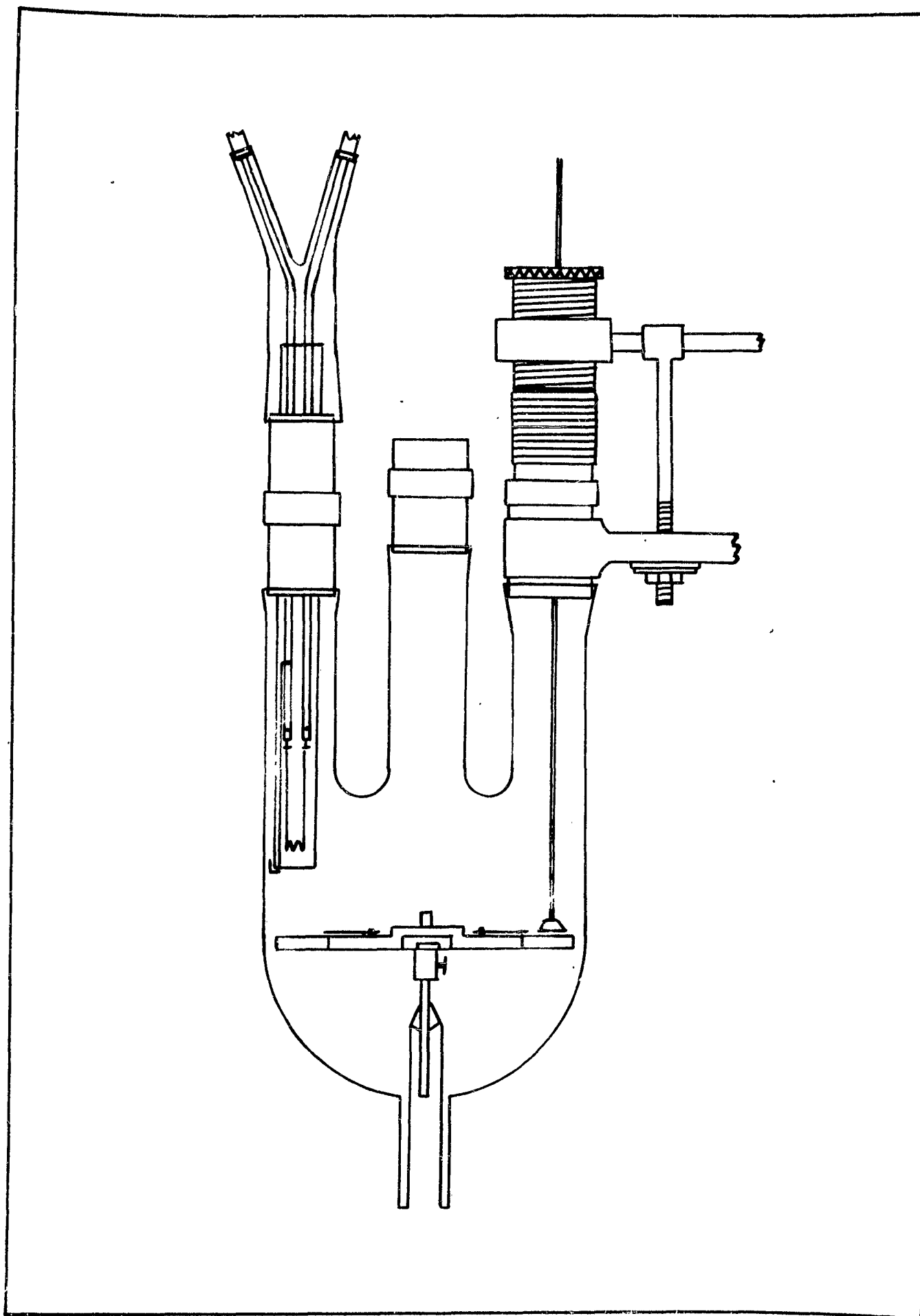


Figure 1

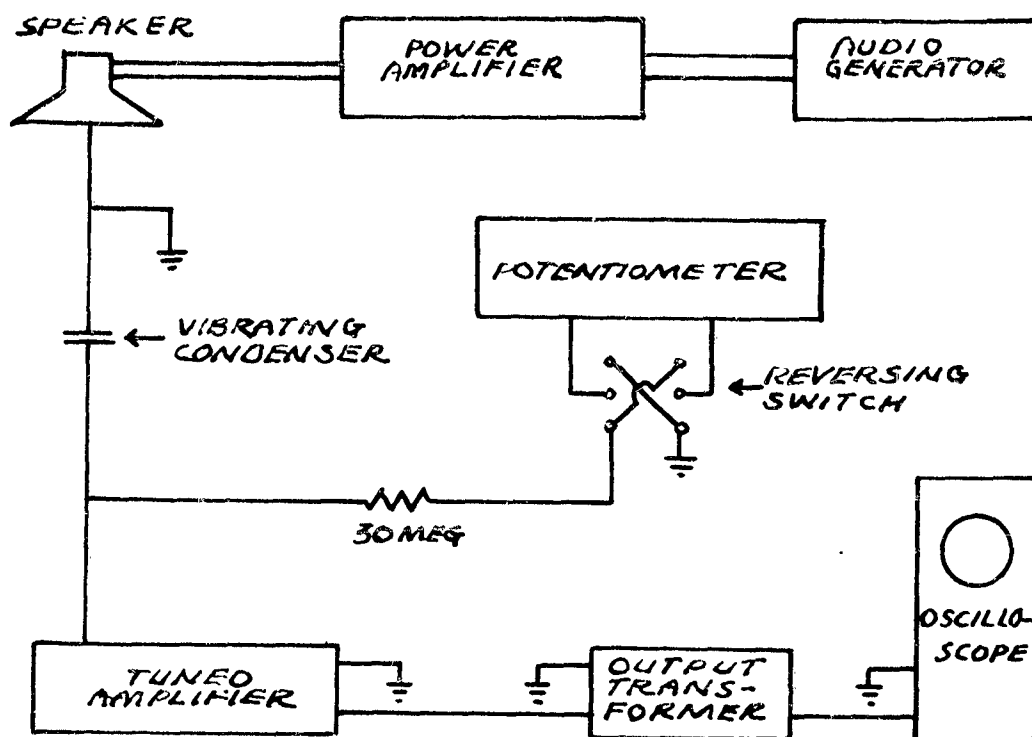
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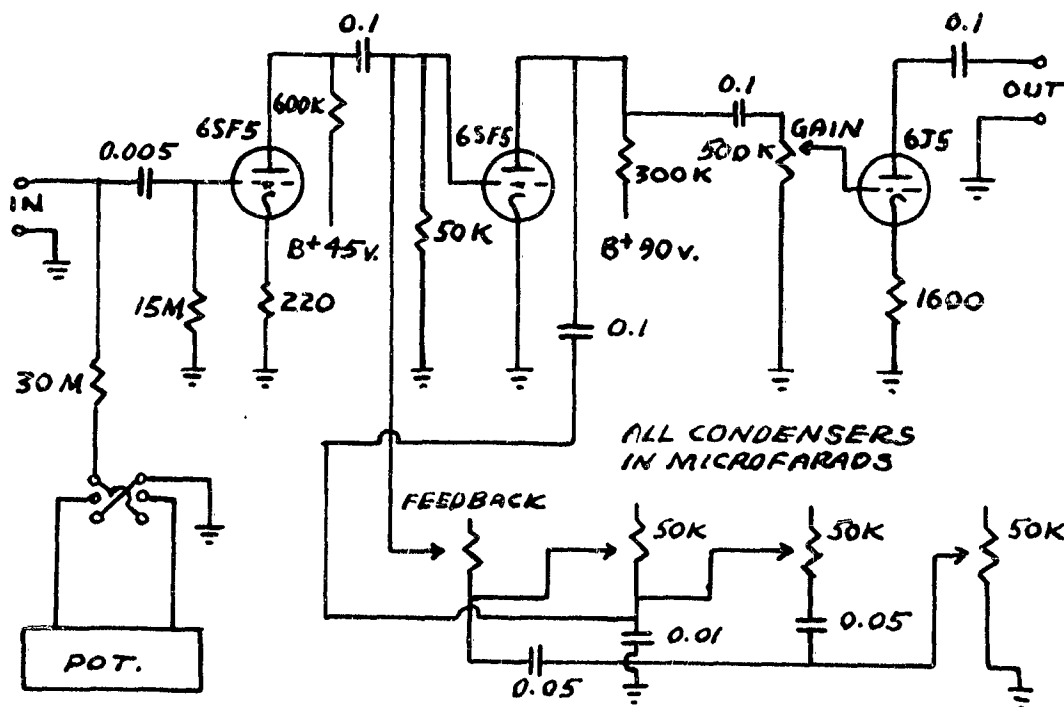
Table 1

Materials Used

Material	Form	Original Purity, %	Purification Treatment	Spectrographic Anal. of Films, Approx. % of Impurities
Oxygen	Commercial	99.5	Dried	----
Nitrogen	Commercial	99.5	Oxygen removed with Vanadyl Sulphate Soln., Dried	----
Water	Distilled	----	Distilled from Alk. Permanganate, Boiled to Remove Gases	----
Aluminum	Wire	99.7	Outgassed before Evaporation	Si, Fe, 0.10 Cu, trace W, none
Iron	Wire	99.8	"	Cr, Mg, Mn, Si, heavy trace W, Al, Cu, Sn, trace
Chromium	Electro-deposited	----	"	Fe, Cu, trace W, none
Nickel	Wire	99+	"	Fe, Mn, Mg, Cu, 0.10 B, Cr, Ca, Ag, W, trace
Lead	Sheet	----	"	Ni, Mn, Ag, 0.01 Cu, Fe, B, trace



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for evaporated metal films be thoroughly outgassed so that contamination of the film is avoided (17, 26). The oil-pump fluid was also outgassed at this time by heating.

5. After several hours of outgassing, the heating mantle was removed and the vacuum system was flushed several times with dry, oxygen-free nitrogen. This removed any active gases that were baked out of the metal parts, and left a low residual of oxygen in the system.

6. The oil pump was brought up to operating temperature, and the system was pumped down to a few microns before cooling the traps. The system was pumped overnight with dry ice and alcohol in the traps. Liquid nitrogen was used prior to, and during the experimental work in most cases.

7. After the system was evacuated, the filament was outgassed by successive heatings as described before. The system was then left to pump down to its lowest pressure.

8. A film was evaporated, the cross-bar was swung around with a magnet, and the platinum reference was adjusted as close as possible to the newly evaporated film. Measurements started about one minute after evaporation. The contact potentials were measured as various gases were admitted and withdrawn.

Water vapor was difficult to manipulate in the vacuum system, because of its low vapor pressure. If liquid nitrogen were used for the cold traps, water vapor could be admitted and closed off with the ground-glass seal at about 5×10^{-4} mm. If dry ice were used for the traps, water vapor could be admitted to several microns, but the vapor pressure from ice in the cold traps at this temperature always caused a virtual leak. Thus the system could not be pumped down again without thawing out the cold traps. For these reasons, the pressures of water vapor were limited to lower ranges than those used for the oxygen and nitrogen.

9. On completion of the experiment the microscope slide-covers were removed, cleaned with water and acetone, dried in the desiccator, and weighed. The new portion of evaporated metal was then scraped off, and the slide-cover was cleaned, dried, and reweighed. The film thicknesses were estimated from the bulk density of the pure metal and the area covered. The weighings were made on a microbalance with a sensitivity of five micrograms. Blank determinations indicated an accuracy of ± 10 micrograms for this method.

The work of Bartlett and Ball on thickness measurements of evaporated metal films indicates that the weighing method is satisfactory (27). With silver deposited on cover glasses, they obtained good correlations between thicknesses obtained by double-beam interferometry and by weighing.

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Tests on the Experimental Method.

It was of interest to know whether or not the distance of separation of two metal surfaces had any effect on the measured contact potential between the two. A contact potential apparatus utilizing a microscope assembly was used for such measurement. These were done in air. The fine adjustment screw was calibrated so that the distance of separation of the surfaces could be measured accurately. The potential-distance effect found with this apparatus is shown later.

A number of preliminary tests were made with bulk metals to ascertain the effect of gases on the platinum reference during the experimental runs. For this work sheet aluminum, gold, and platinum (the reference) were used; the gold and platinum were of laboratory grade and the aluminum was of commercial grade. The metals were installed in the contact potential apparatus and the system was evacuated overnight before the tests. Heating of the metals was avoided because it caused a gradual drift of contact potentials from run to run; this was especially noticeable in the potential between two gold surfaces. This difficulty was also found by Anderson and Alexander (13) where the potential between two gold surfaces changed for a number of experiments because of the heating of one of the plates.

After the bulk metals were pumped overnight, air was admitted to the vacuum system and pumped out as was done in the experiments with the evaporated films. Thus a direct comparison was made between the effect of gases on the bulk metals and the evaporated films.

The data were plotted such that potentials in ascending order on the scale corresponded to film potentials more active than platinum; this meant that the film had a lower work function than the platinum. Potentials in descending order represented films more noble than platinum; here the work function of the film was greater than that of the platinum. For example, in Fig. 9, the iron film went from an initial potential more noble than the platinum to a final potential more active than platinum. This corresponds to an initial work function greater, and a final one smaller, than that of the platinum.

Results

The System of Measurement.

It was found that there were variations in contact potential because of different positioning of the two surfaces relative to one another. When one surface was rotated with respect to the other, and potential readings taken every 45°, a potential range up to 0.06 v. was found. If the angle

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between the surfaces was varied, potential differences of about 0.06 v. were observed also. The first variation indicates that the potential between closest points makes the largest contribution to the over-all potential, and that the surfaces are non-homogeneous. The second variation noted could be due to an edge effect.

Uhlig has investigated the contact potentials of alloys and mixed patches of metals (7). He found no linear relation between the work functions of two metals and the work function of their alloy. On the other hand, two metals placed adjacent to one another to form a continuous surface contributed to the contact potential in direct proportion to their respective areas. Uhlig concluded that contact potentials by the vibrating condenser method are an average potential of all surface patches.

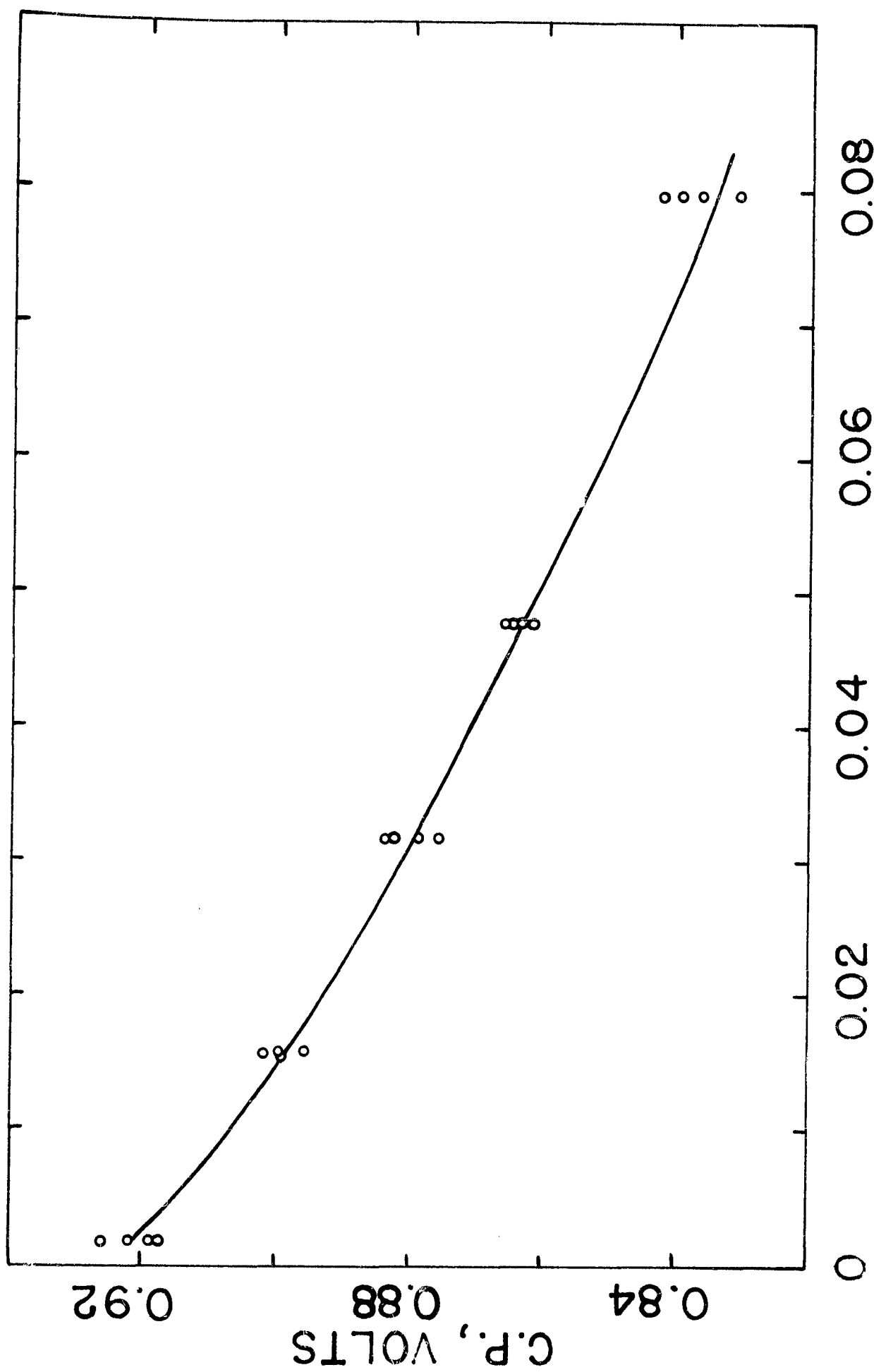
A regular variation of contact potential with distance of separation of the surfaces was found. Fig. 3 shows the results the contact potential of aluminum and brass vs. minimum distance of separation. Since one of the surfaces was vibrating up and down, the distances shown are minimum distances of separation. With like metal the potential passed through zero and the change was more nearly linear.

The amplitude of vibration is also a variable. A potential variation of 0.03 v. was found by changing the amplitude of vibration through a range of about 0.04 to 0.06 mm. Potential-distance variations of about 0.05 v. were observed by Uhlig, using a similar type of apparatus (7). In both his work and this there was no effect of frequency of vibration.

During the experimental work with evaporated films, the distance between the film and the reference was made as small as possible, and this position was fixed during the course of each experiment. Thus none of the variables listed above entered significantly into the results, but small potential changes may have occurred from thermal expansion of the apparatus. This accounts, for example, for the slight downward drift of the Au vs. pt curve in Fig. 4.

Stability of the Platinum Reference.

The contact potentials of bulk metals with aged surfaces were unaffected by exposure to air, as seen from Fig. 4. The various series were run under the same experimental conditions that were used for evaporated films. These results are in agreement with the diminishing effect of oxygen and air on the evaporated films as they aged (see Fig. 8). Thus it appears that the use of the platinum reference is satisfactory for the environments used.



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Figure 3

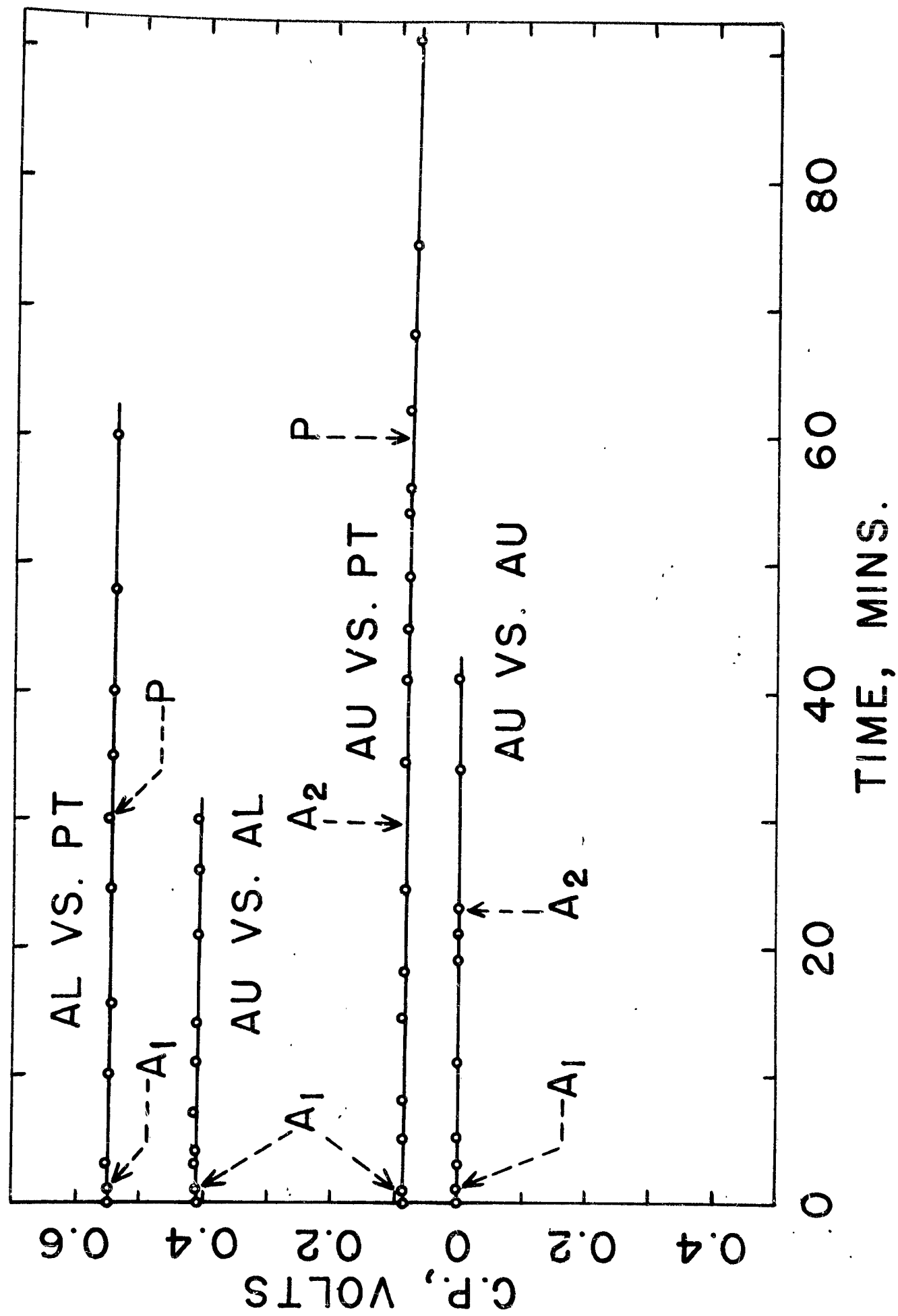
Figure 4

Contact potentials between bulk metals,
on admission of air to system after
pumping overnight

A_1 - air admitted to 0.04 mm.

A_2 - air admitted to 0.10 mm.

P - system pumped



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The contact potential between two freshly cleaned gold surfaces was zero, and air had no effect on it (Fig. 4). This value was not obtained inevitably because of some difficulty in keeping the surfaces uncontaminated.

The platinum references were subjected to heating and outgassing treatments for each experiment, and therefore its work function probably changed somewhat. However, there is no reason to believe that the work function of the reference changed significantly during the course of any one experiment, and this was critical period for constancy.

Aluminum Films.

Results with aluminum films are shown in Figs. 5 and 6. The potentials became more active with time so the work function decreased as the metal was oxidized by the residual oxygen in the vacuum system. This is contrary to what might be predicted, since massive oxidation of a metal has been shown to increase the work function (7).

Fig. 5 shows that pure nitrogen had no effect on the above process. However, adsorption of nitrogen was detectable after the film had reached a stable potential. The potential change because of nitrogen reversed itself while the gas was still in the system. It was decided that this was caused by a temperature drop as the gas entered the system under a pressure gradient. The gas was adsorbed as it entered the system and desorbed as it warmed to ambient temperature. To check this nitrogen was allowed to enter the system through a capillary leak over longer periods of time, to reduce the cooling effect. The potential dip then disappeared (Fig. 5).

Nitrogen adsorption gave the aluminum film a more noble potential. This was found true of reversible adsorption in all these studies with few exceptions.

Admission of air (Fig. 6) shows the effect of oxygen adsorption on the aluminum films. The potential decreased at first but the over-all change was to a more active potential, as was found with other films. In other words the adsorption of the oxygen temporarily increased the work function of the aluminum, but the final effect was to lower the initial work function. After the film reached a stable potential, adsorption of oxygen lowered the film potential by a definite amount. This process was reversible and is believed to be an effect of physical adsorption on a lightly oxidized surface.

The downward drift of potentials in the last part of Fig. 6 was due to the slowness of desorption of the oxygen. It was shown on other films that pumping overnight would bring the potential back to the original peak value.

Figure 5

Contact potential between evaporated
aluminum film and platinum

N - nitrogen admitted to 0.04 mm.
N₁ - admitted instantaneously
N₂ - " gradually, less than 1 min.
N₃ - " " , 4 min.
N₄ - " " , 50 min.
P - system pumped

Film thickness about 300 Å.

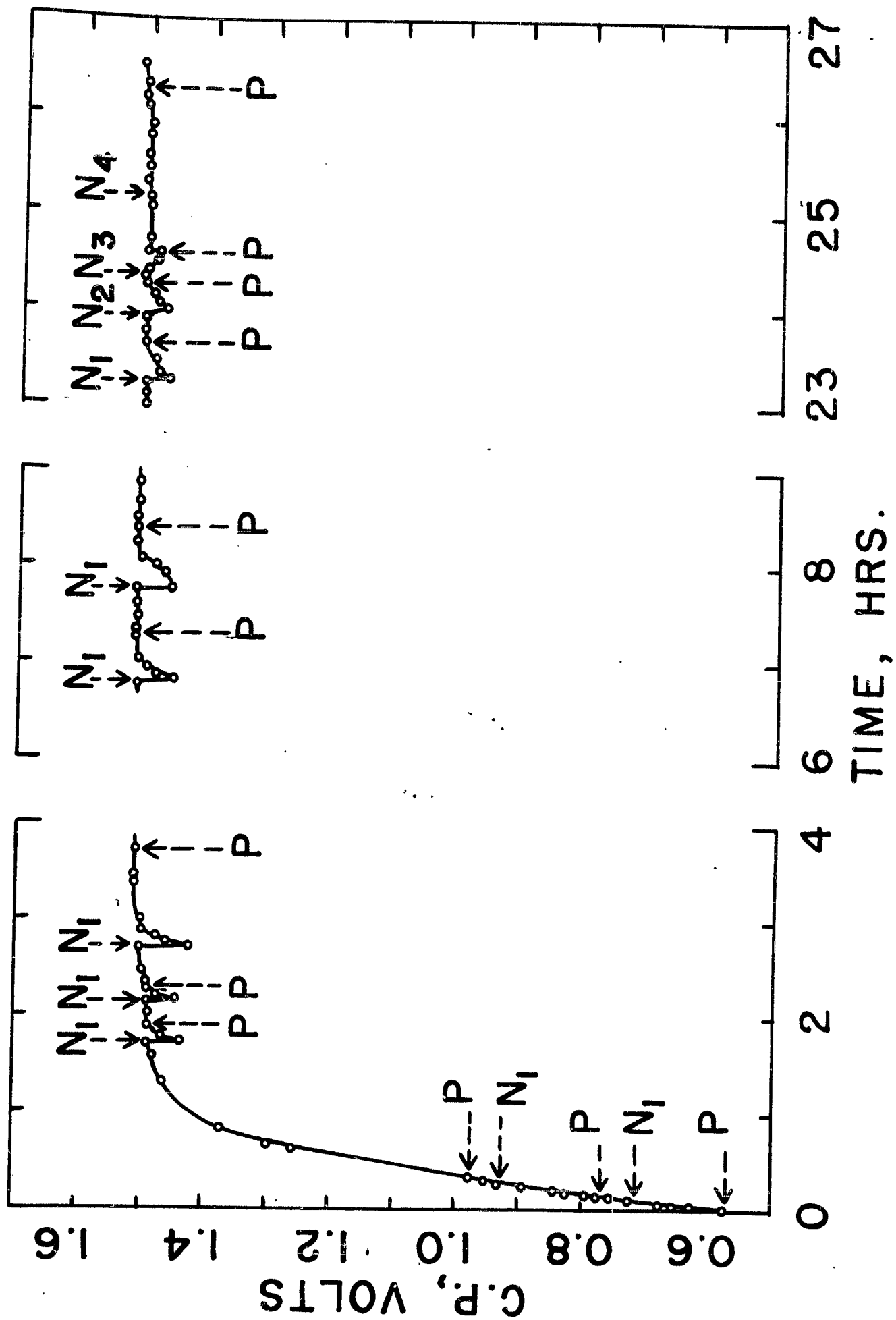


Figure 6

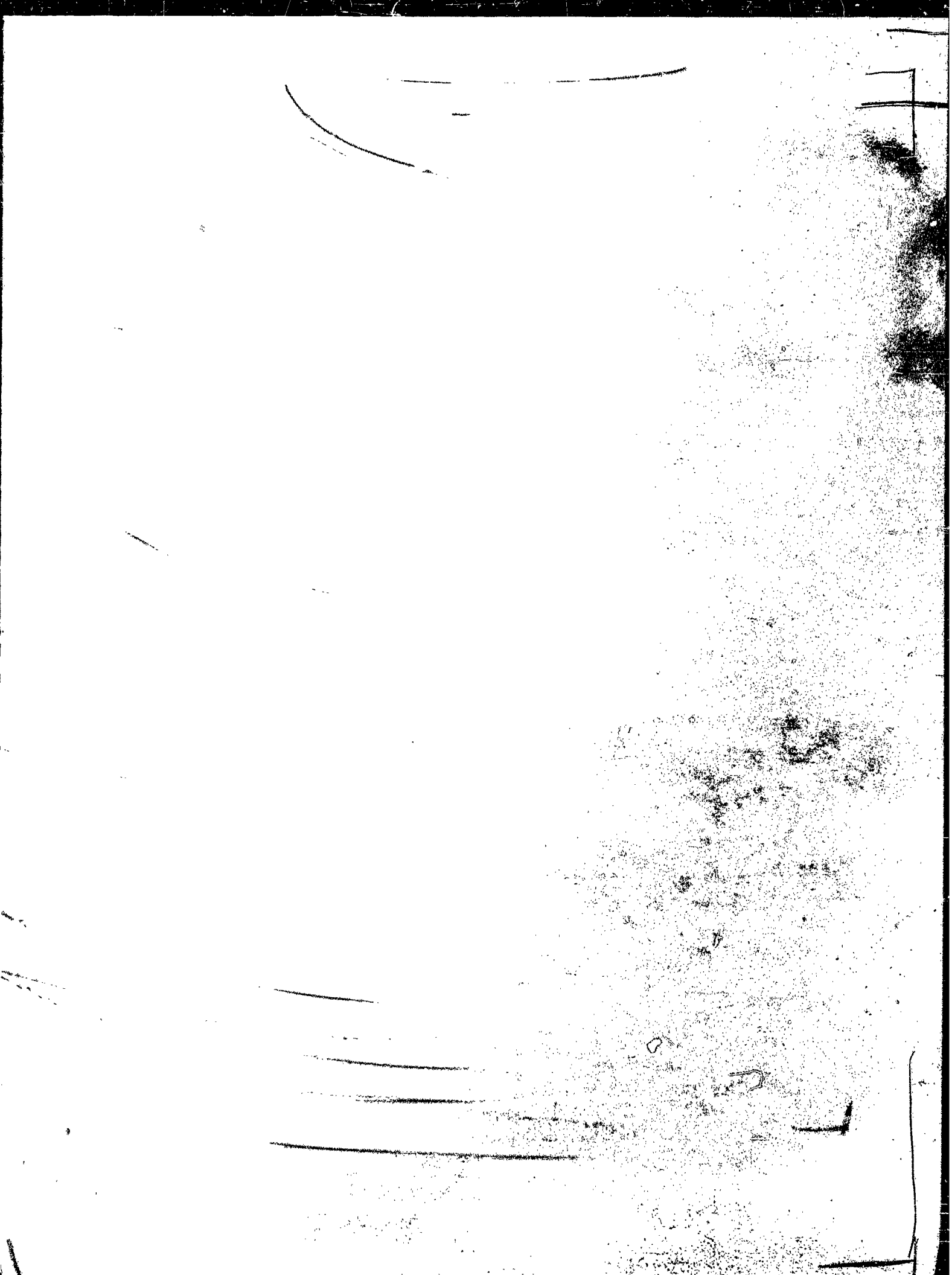
Contact potential between evaporated
aluminum film and platinum

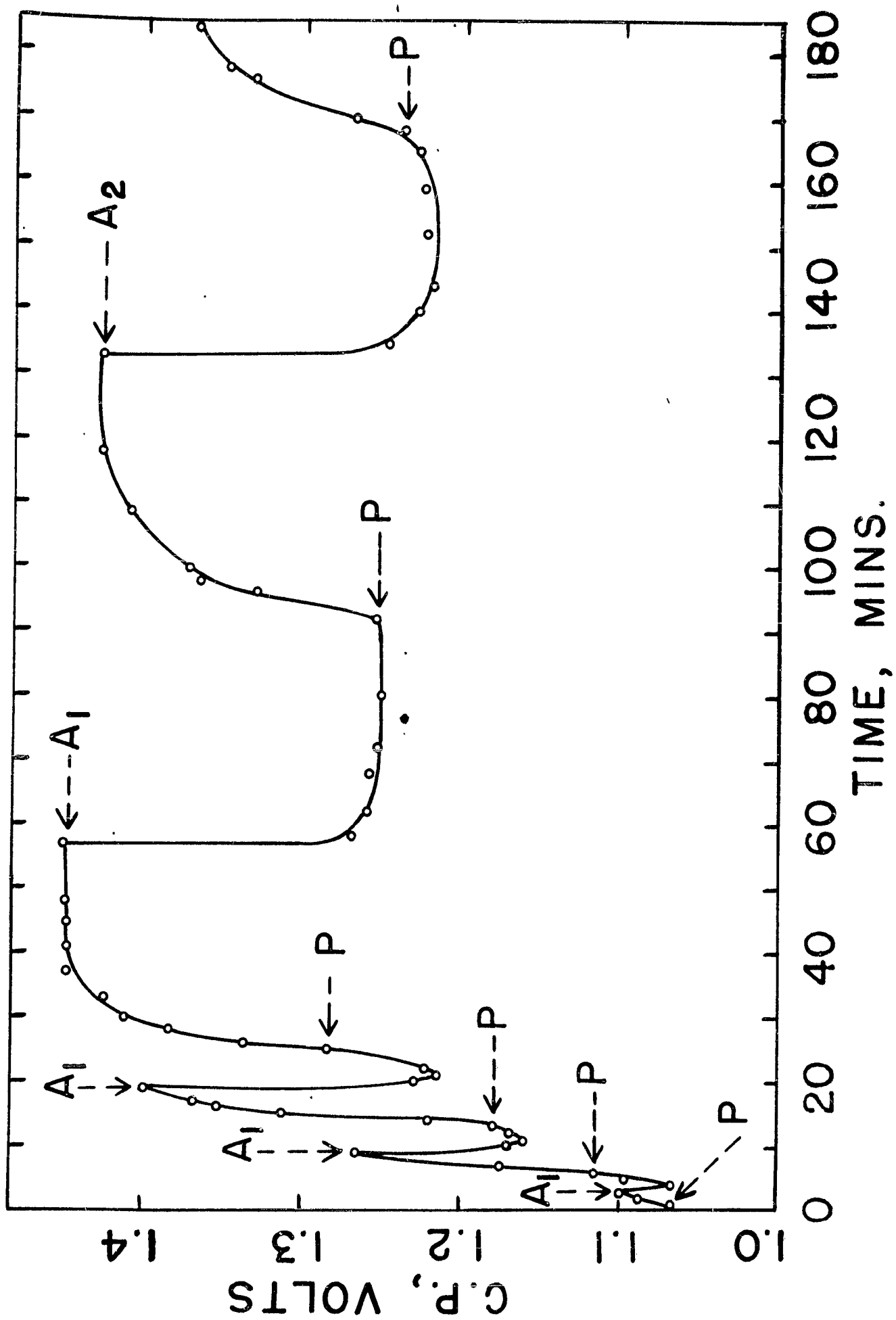
A₁ - air admitted to 0.04 mm.

A₂ - air admitted to 0.16 mm.

P - system pumped

Film thickness about 700 Å.





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Another aluminum film was evaporated on top of the one used to give the data of Figs. 6 and 7 and exhibited essentially the same characteristics. This rules out the possibility of any effect of the glass substrate on the reactions of the films.

Water vapor had no measurable effect on aluminum films at 5×10^{-4} mm.

Others also found a decrease in work function of fresh metal surfaces during the initial oxidation process, and some also found the latter decreased as the oxidation became more massive. Von Fianda and Lange (15) found that the work function of freshly abraded aluminum and other metals decreased initially. Several of the metals showed a very slow increase of work function later as the surfaces aged. Giuer and Lange (16) found that heating abraded metal surfaces at 300° C. in a low pressure of oxygen increased the work function; gold, platinum, palladium, and cadmium were used. Daniels and Colby found an initial decrease of the work function of a freshly cleaved zinc crystal (11). Jones and Morgan found that a thin "tarnish" 10 to 20 Å thick increased the field emission from a metal surface (28). Cashman and Huxford (29) found that a small dose of air increased the photoelectric emission from magnesium. Larger amounts of air decreased the emission below the value before any air was added. Burstein, Surova, and Zaidenman reported that the work function of evaporated iron films originally decreased on oxidation, but later at elevated temperatures it increased (30).

The aluminum films reached a stable potential of about 1.5 v. within a few hours. This reflects the characteristic high stability of aluminum oxide. Boetcher and Haas found that the oxide film on evaporated aluminum did not exceed 40 Å after two months. Aluminum films 300 Å thick had the same specific resistance as that of the bulk metal (31).

The potential of 1.5 v. agrees with the value of 1.47 v. reported by Uhlig for the potential between evaporated aluminum and abraded platinum (7). The potential between abraded platinum and abraded aluminum was smaller, 1.29 v.

No correlation could be found between contact potentials and film thicknesses of the aluminum, in the ranges studied. A compilation of such data is shown in Table 2. The final potentials shown are lower in some cases because the films were not all aged for the same length of time. The variations in initial potentials are considered to be due to the different stages of oxidation of the films when the first potentials were measured; a small difference would also result from effect of positional adjustment.

Figure 7

Contact potential between evaporated
chromium film and platinum

N - nitrogen admitted to 0.04 mm.

A - air admitted to 0.05 mm.

P - system pumped

Film thickness about 250 Å.

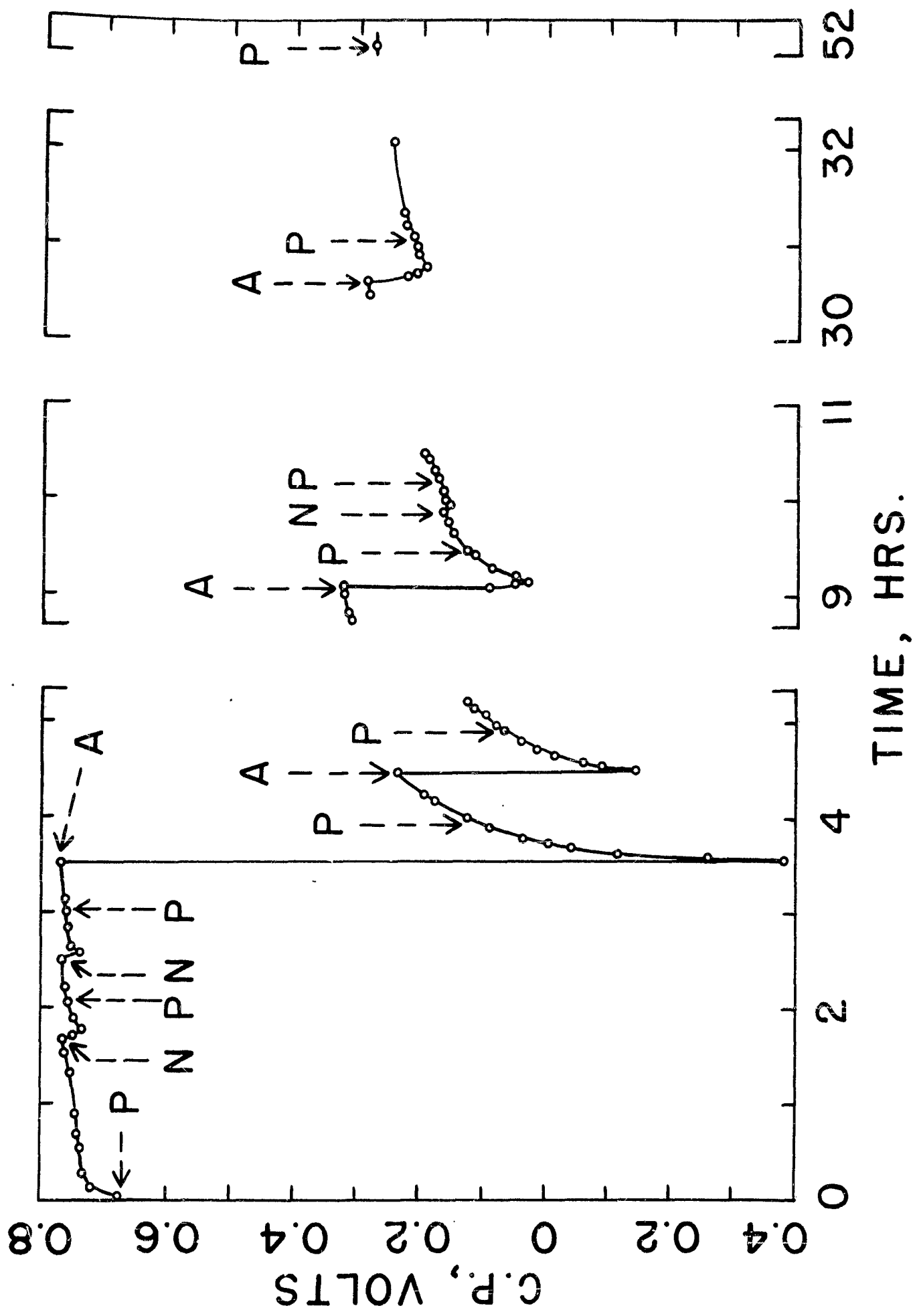


Table 2

Evaporated Aluminum Films

<u>Film No.</u>	<u>Thickness, Å</u>	<u>Orig. C. P.</u>	<u>Final C. P.</u>	<u>Hours Elapsed</u>
1	280	0.577	1.514	24
2	620	0.852	1.400	24
3	695	0.714	1.024	1
4	710	1.067	1.424	2
5	792	0.675	1.484	7
6	1400	0.760	1.362	8
7	2130	0.670	1.301	3

A series of four aluminum films from 660 to 1530 Å thick were examined under a stereoscopic microscope. The superficial appearance of the films was the same, except that the thinnest film had a more granular surface. All the films had tiny holes, rather evenly distributed.

Chromium Films.

Chromium films exhibited active, stable potentials initially, as shown in Fig. 7. The admission of air or oxygen quickly reduced the potentials to passive values, while nitrogen and water vapor had little effect. This and subsequent data on nickel and iron films gave a substantial proof that such passive states were due to an adsorbed layer of oxygen. The increase in work function that corresponds to the passive state is believed to be due to the effect of oxygen ions at the surface. It has been shown that a monolayer of oxygen increases the work function of a tungsten filament by 4 to 5 e. v. (9).

After exposure to oxygen, chromium films showed more active potentials during the subsequent oxidation process. Fig. 7 shows that oxygen had less and less effect on the film as it aged, in agreement with the lack of potential changes found with bulk metals.

The drop in potential caused by admission of air reversed itself before the air was pumped out for two reasons. First, the temperature of the gas was increasing, since it had been rapidly cooled by expansion on entering the system. Second, the pressure gradually dropped during

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this time due to adsorption of the gases, and because of the pumping action of the Phillips gage. It was found in later experiments that more stable pressures could be retained by turning the Phillips gage off before admitting gas samples, and using the Pirani gage for this pressure range. The reversal could also be stopped by admitting another charge of oxygen.

In Fig. 7 the final potentials are less than the initial ones; this corresponds to an over-all increase in work function in going from an unoxidized to an oxidized film.

The thicknesses of the chromium, nickel, and iron films were all about the same, so no correlations between thickness and contact potential could be made. The thickness was limited by the capacity of the evaporating system. The films used were obtained by two or three evaporations over a total period of several minutes. Evaporations longer than a few minutes were not feasible since the associated metal and glass parts got too hot and caused the pressure in the system to rise. At higher pressures, the evaporation rate became diminishingly small.

Nickel Films.

Nickel films gave inconsistent initial results in that they sometimes showed active potentials and other times noble potentials. Fig. 8 shows the former. The film responded to oxygen in the same way as did chromium films, except for a slower rate of change.

Oxygen showed less and less effect on the potentials as the nickel films aged, as was true of chromium films. The nickel films were all about the same thickness, yet initially were found in different potential ranges; evidently residual oxygen in the vacuum system was the determining factor. The final potentials of the film were typical of bulk metals.

Iron Films.

The iron films exhibited very passive potentials at first. In Fig. 9 the film started at a potential over 0.7 v. more noble than the platinum. Comparison to the chromium and nickel films indicates that the iron was covered with a layer of oxygen when the first potentials were measured. Dushman has shown that all types of bulk iron contain significant amounts of oxygen (32); therefore the iron sample itself was a source of oxygen contamination. The film changed to more active potential on reaction with residual oxygen in the vacuum system.

Figure 8

Contact potential between evaporated
nickel film and platinum

N - nitrogen admitted to 0.05 mm.
O - oxygen admitted to 0.06 mm.
H - cold traps warmed to -78°C .
W - water vapor admitted to 0.001 mm.
P - system pumped

Film thickness about 250 Å.

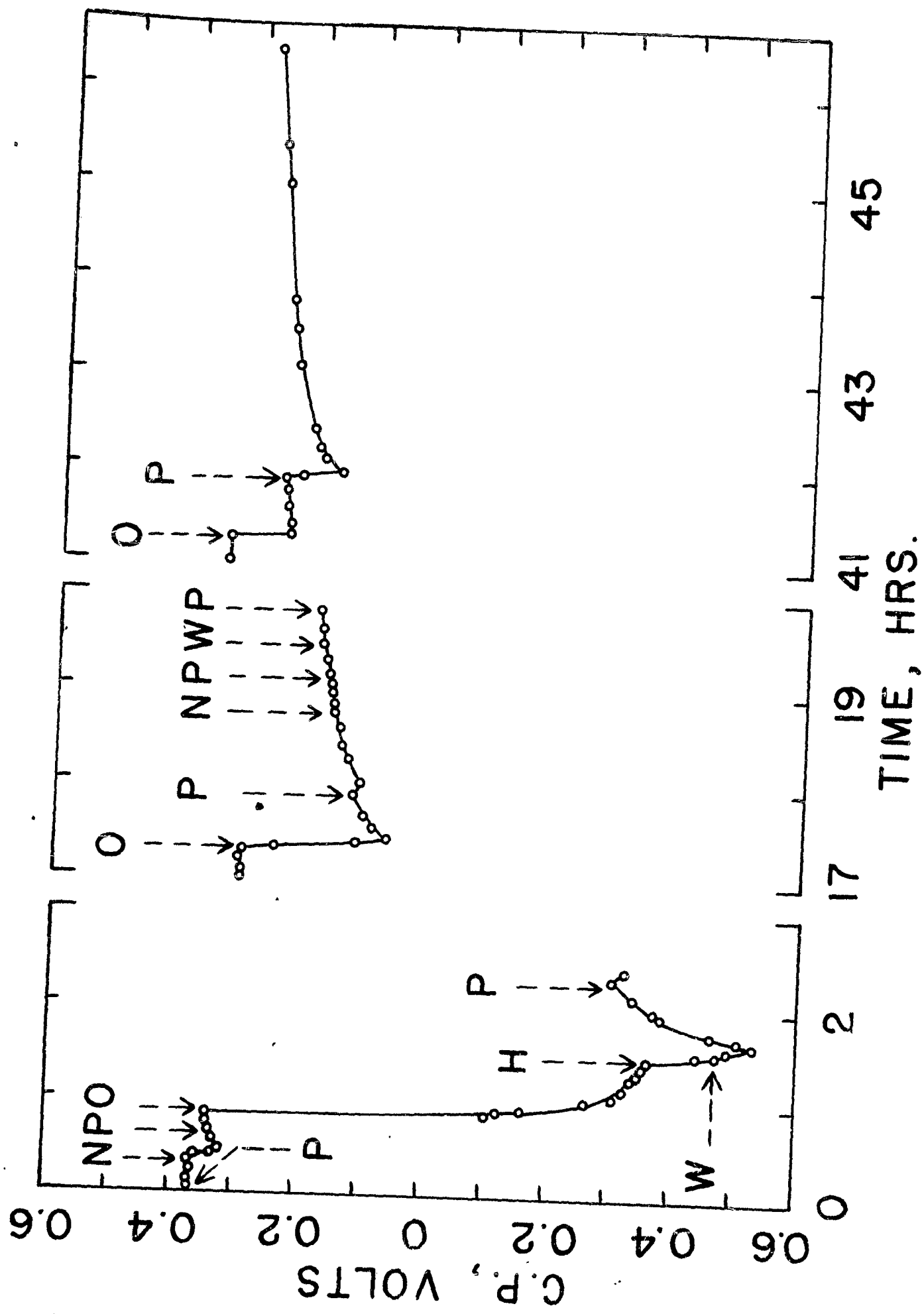
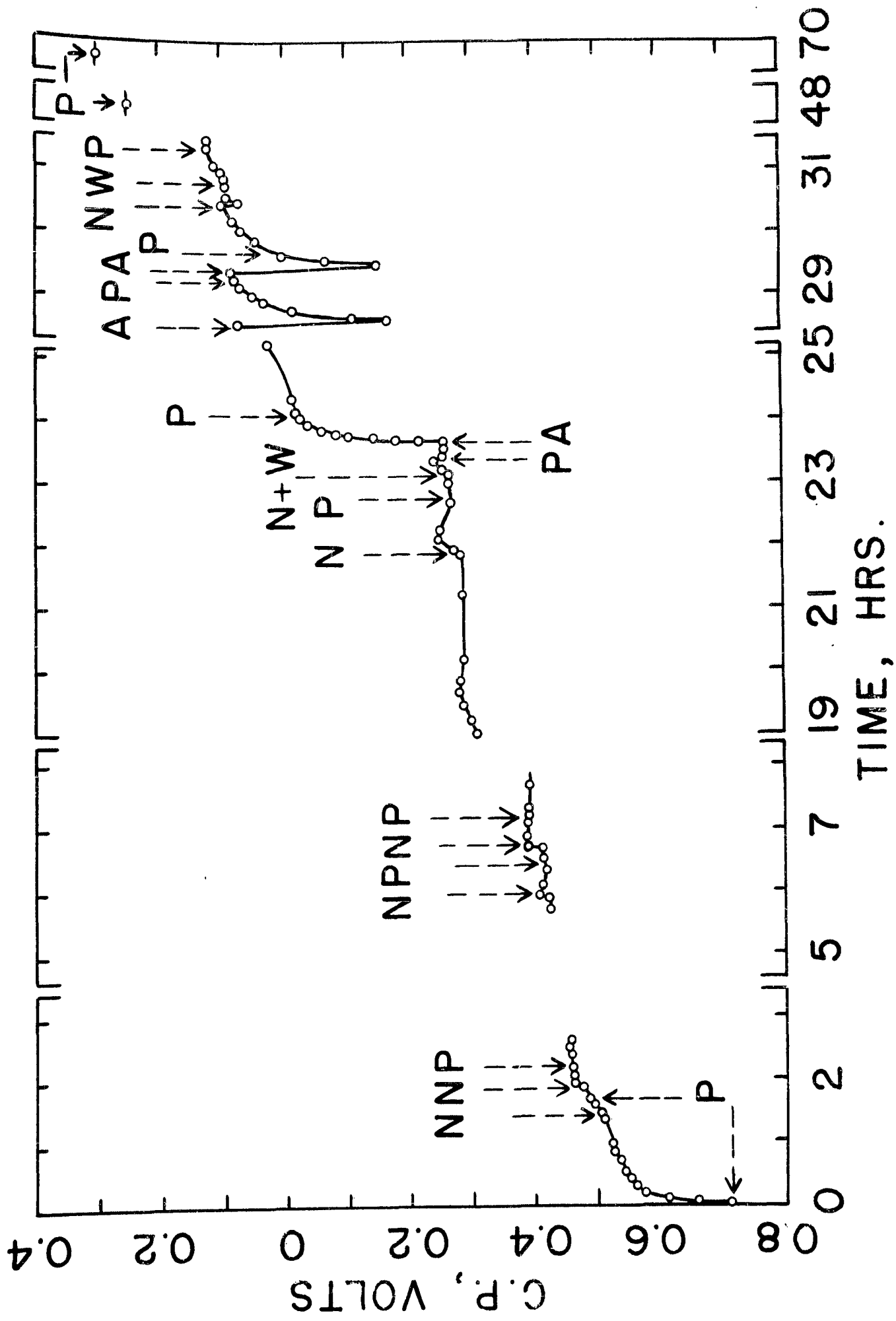


Figure 9

Contact potential between evaporated
iron film and platinum

A - air admitted to 0.04 mm.
N - nitrogen admitted to 0.04 mm.
W - water vapor admitted to 0.002 mm.
P - system pumped

Film thickness about 250 Å.



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Admission of nitrogen and water vapor during this period showed the slight changes in potential that previously have been attributed to physical adsorption. However, the changes were to a more active potential, opposite to that observed on other films, and the first admission of air also caused a rapid rise to a more active potential. Adsorption on the film after 29 hours produced noble potentials and was typical of the reversible adsorption found on other metal films. It appears that the first adsorption of nitrogen may have increased the potential because of oxygen present in this experiment. The first addition of air evidently caused a rapid oxidation of the film, similar to the process with aluminum. Later admissions of air were then typical of reversible adsorption on a lightly oxidized surface. These potential drops reversed themselves before the air was pumped out, as with the chromium films. This was evidently due to the temperature rise and the pressure drop that was taking place as discussed earlier.

Fig. 10 shows similar effects. In this case nitrogen and water vapor had no noticeable effect on the film. The film was exposed to the atmosphere before the final measurement shown; the potential of 0.45 v. agrees with the value of 0.46 v. that Uhlig found between an evaporated iron film and abraded platinum (7); his value for abraded iron and abraded platinum was 0.49 v.

Burstein, Surova, and Zaidenman found that the work function of iron films decreased during the initial oxidation process (30). However, subsequent heat treatment caused the work function to increase again as more massive oxidation followed. All of the metal films used here retained a metallic luster during and after the experiments. The dry metal surfaces showed an insignificant oxidation rate at room temperature, as seen by the stability of the final contact potentials.

Lead Films.

Lead films were used in order to study a non-transition metal with a higher work function than aluminum, yet one that is not a noble metal. They showed the general characteristics of the aluminum films; no passive states were observed.

Fig. 11 shows no effect by nitrogen but a rapid rise in potential by oxygen. This was followed by a drop, indicating that rapid oxidation followed by physical adsorption had taken place. This is evident from the reversible adsorption effects measured after the film had aged a few hours. The last addition of oxygen caused a relatively large drop in potential. This may be attributed to the fact that the film had been pumped for a long period of time before this final addition of oxygen.

Figure 10

Contact potential between evaporated
iron film and platinum

- N - nitrogen admitted to 0.04 mm.
- W - water vapor admitted to 1×10^{-4} mm.
- A - air admitted to 0.04 mm.
- P - system pumped
- P₁ - system pumped after exposure of film
to atmosphere

Film thickness about 250 Å.

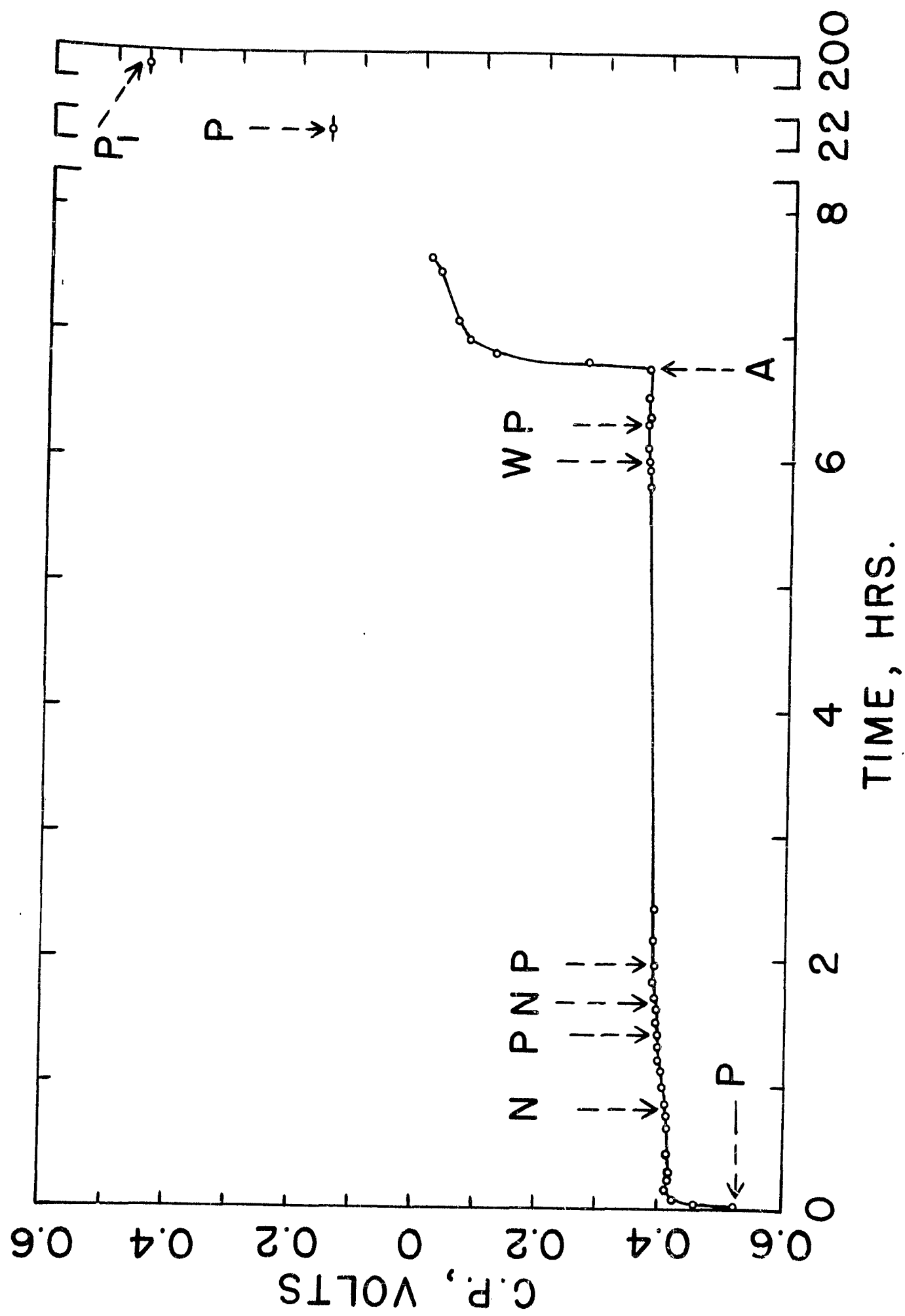


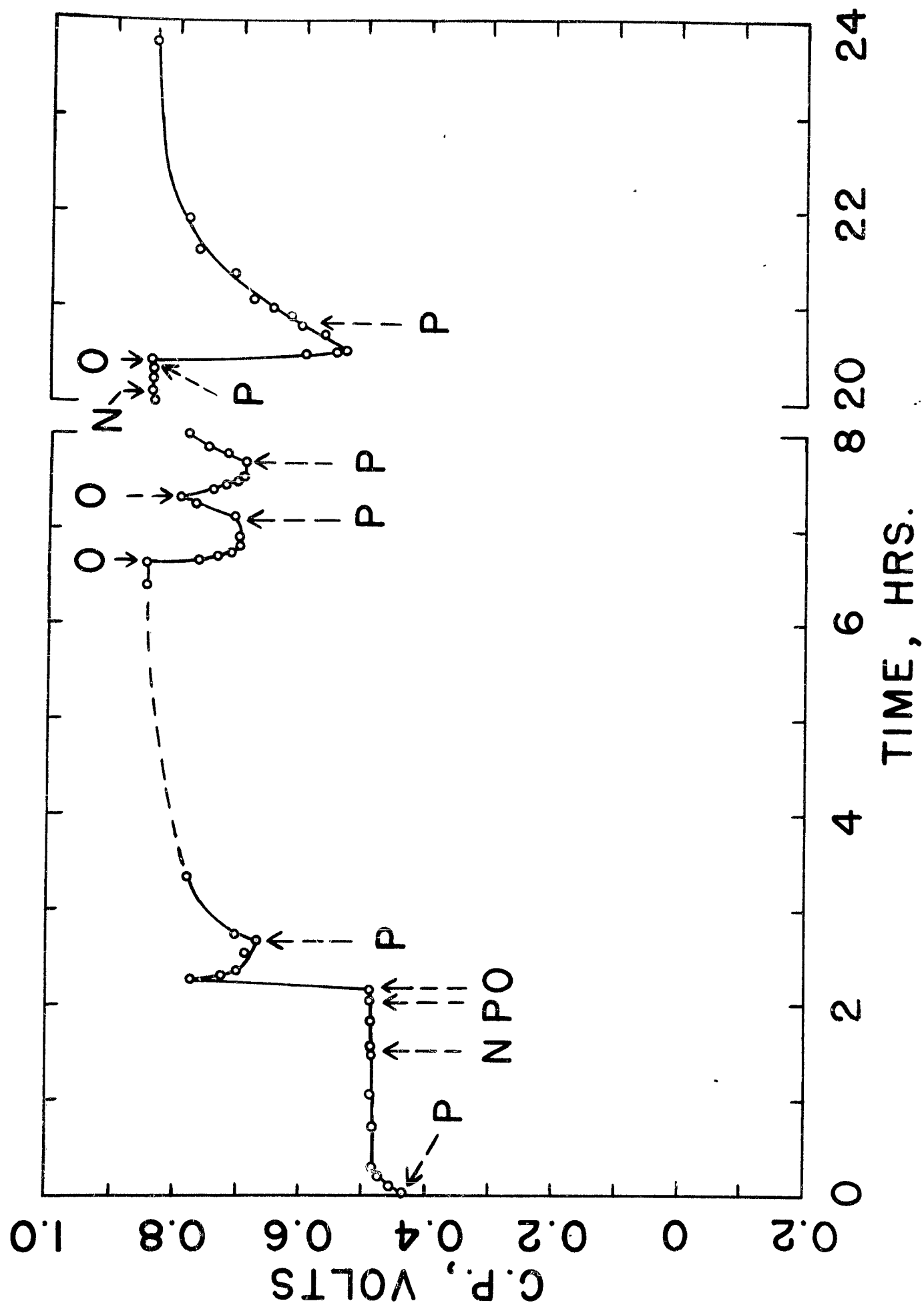
Figure 11

Contact potential between evaporated
lead film and platinum

N - nitrogen admitted to 0.04 mm.

O - oxygen admitted to 0.05 mm.

P - system pumped



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As this film (estimated to be 500 Å thick) was washed with water, the usual procedure before drying and weighing, it turned milky white and washed off of the glass substrate. Lambert and Cullis found that freshly purified lead reacted very rapidly with water and oxygen to form the hydroxide. Distilled lead did this when freshly prepared, but after aging in air for several days, it was not very reactive. They believed that this was due to an allotropic modification of the lead as it aged (33).

The effect of oxygen and water on freshly purified lead is of value in explaining the results on Fig. 12. Water vapor was admitted first, and then the admission of oxygen caused a rapid potential rise similar to that shown in Fig. 11, but to a lesser degree. After 20 hours, the potential of the lead film had become more noble, and the effect of oxygen was small and easily reversible. A comparison of the potentials in Figs. 11 and 12 shows that extensive oxidation of the lead film took place, causing an increase in the work function of the metal. This was the only case where water vapor had any noticeable effect on the oxidation of a film. The thickness of this film was evaluated by omitting the usual washing procedure.

Discussion

The potential-distance effect found in this work was also reported by Uhlig (7), who used a similar type of apparatus. However, Zisman, who introduced the vibrating condenser method, stated that measured potentials were independent of the position of the surfaces (20). Koenig has pointed out that compensation methods for contact potentials are based on an unproved assumption. He states that there is no phenomenological principle which requires the compensation potential to be equal to the Volta potential (21).

The potential-distance variation found indicates that the vibrating condenser method is contingent on such a variation. The periodic variation of distance produces the alternating voltage detected by the null indicating instrument, and the null potential varies with the mean distance between the surfaces.

Contact potentials were detected with surface separations as large as one millimeter, but the potential-distance measurements were made with a separation of only few hundredths of a millimeter. This indicates that the electrons at the surface of one metal were in the potential field of two metals, rather than one. Such a field would modify the work function of each metal, since the work function includes the distance from inside the metal to infinity. This fact appears to be the reason for the variation of potential with distance that has been found.

Figure 12

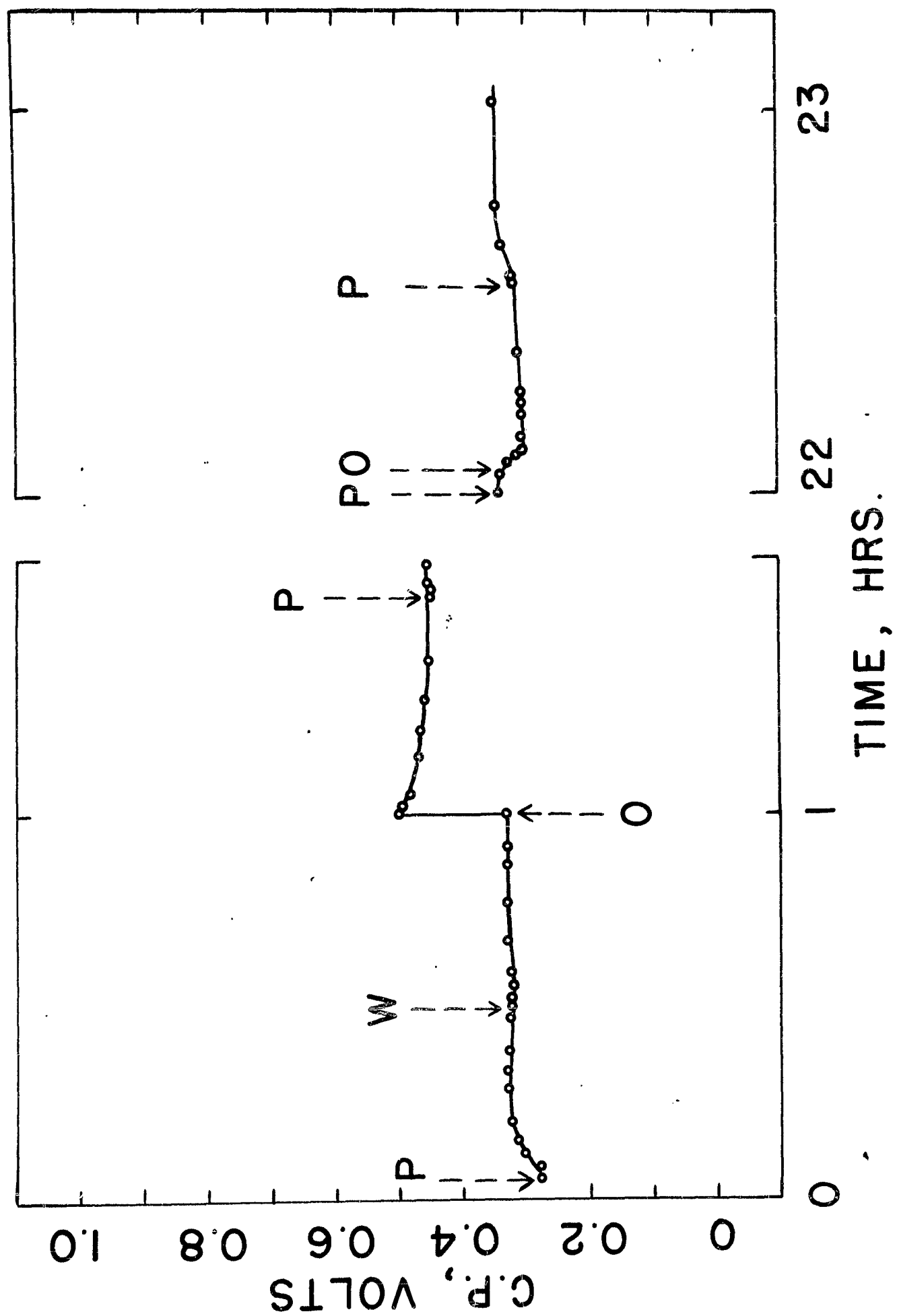
Contact potential between evaporated
lead film and platinum

W - water vapor admitted to 0.002 mm.

O - oxygen admitted to 0.04 mm.

P - system pumped

Film thickness about 500 Å.



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The data on bulk metals show the feasibility of a noble metal reference. It would be necessary to conclude that the bulk metals did not change in work function during adsorption of air, or assume that all metals changed the same amount. Koyen found that adsorption of water vapor changed the work function of bulk platinum (34); therefore there is some doubt about the use of a platinum reference with water vapor.

The range of potentials found with evaporated films show that no measurements were made with a bare metal surface. The work function of oxidized platinum was found by Oatley to be 6.35 electron volts (14). Therefore, the contact potential between a platinum reference and bare metal films would be on the order of two to three volts, with the films at the more active potential. In this work the initial potentials of the films were anywhere from slightly active to more noble than the reference.

The potentials of all the metal films became more active as oxidation took place. This phenomenon is not restricted to evaporated films; it was shown previously that such an effect was found with freshly abraded metals (15) and freshly cleaved metal crystals (11). Similar effects were found in field emission and photoelectric emission (28, 29).

The observed potentials may be explained by regarding the contact potentials as a difference of two work functions as modified by an electric double layer at each surface. The increase in work function due to the initial adsorption of oxygen would be carried by the effect of polarization or ionization of the adsorbed oxygen molecules (or atoms, if dissociation occurs). The adsorption of oxygen on a bare metal surface could lead to the formation of negative ions; this is possible because of the high electronegativity of oxygen and the narrow energy barrier of the pure surface for electron emission. An assembly of such ions would set up a negative space charge which would repel the free electrons in the metal, and in effect increase the work function as is shown presently. Such a state would correspond to the relatively noble potentials that were found with the freshly evaporated films.

The more reactive metals such as aluminum immediately started to form an oxide after evaporation and the observed potential trends followed. As the oxide was formed the negative space charge at the surface becomes diluted with positive aluminum ions. This would cause the potential to rise toward one more characteristic of bulk metals as observed. The oxide growth of aluminum became diminishingly small after a relatively small time, due to the stability of the oxide. Adsorption of oxygen on the thin oxide surface also resulted in an increase in work function, but probably via a different mechanism. Here the double layer is thought to be composed of adsorbed molecules or atoms which are polarized with the negative side out. Other metals showed the effect of continued oxidation, in that oxygen adsorption has a diminishing effect on the potentials,

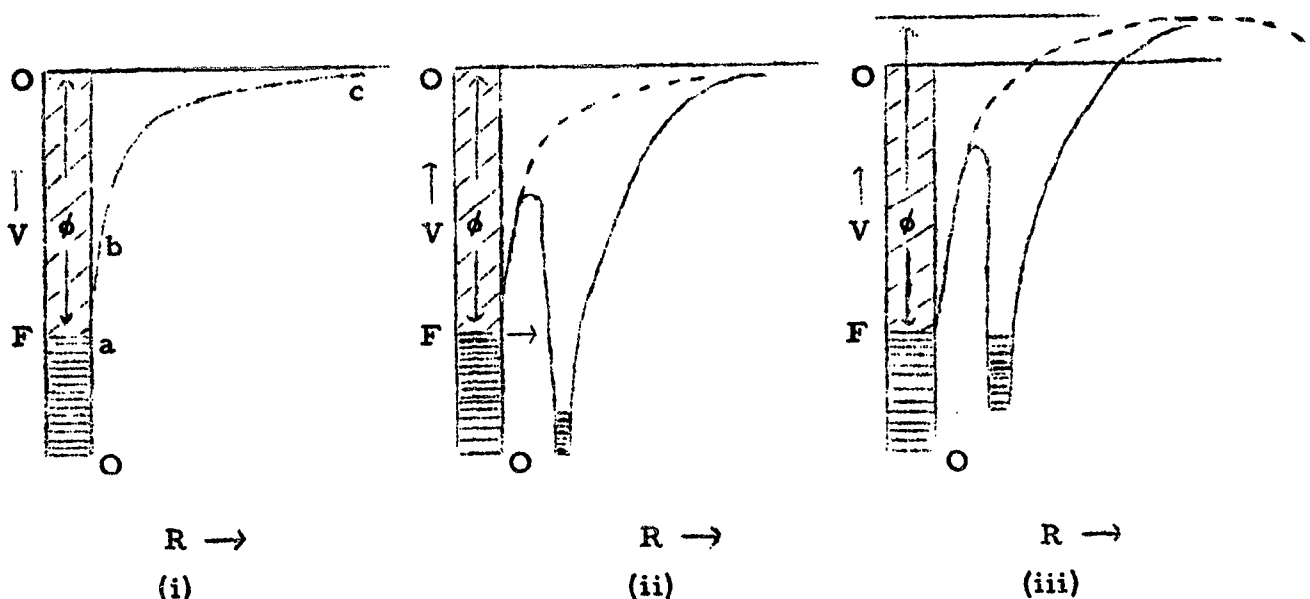
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i.e., the polarization effect was not as great on thicker oxide films. More massive oxidation produced a permanent increase in the work function due to growth of the energy barrier for electron emission. This final development was not observed in this work, but has been reported by numerous other workers (7, 14, 16, 23, 35, 36).

The potential trends of the chromium films showed that relatively little oxygen had been adsorbed before the first measurements. The initial active potentials immediately dropped more than a volt when air or oxygen was admitted to the system, as shown in Fig. 7. Chromium was the only metal that was electrodeposited on the tungsten filament. The evaporated chromium was found spectroscopically pure, and the only likely gaseous impurity in the electrodeposited metal is hydrogen. Most of this hydrogen was removed before evaporation by the preliminary outgassing treatments. The iron samples used probably contained oxygen, according to data on iron collected by Dushman (32). This could account for the initial noble potentials of the iron films.

The noble potentials of the chromium, iron, and nickel may be explained by the effect of oxygen ions on the work function of the metal as shown below.



Here V is the potential energy of the electron, represented as negative in the metal and zero outside the metal. The positive field acting on the electron consists of atomic forces in a range shown as ab , and the electron image-force, shown in the range bc . R is the distance from the surface of the metal, F is the Fermi level in the metal, and ϕ is the work function. The presence of oxygen provides a potential well outside the metal, and electrons ionize the oxygen by tunneling through the potential barrier as shown in (ii). The resulting ions comprise a negative field which repels electrons, and raises the potential barrier and the work function as shown in (iii).

The noble potentials of the transition metals that resulted from oxygen adsorption were relatively stable because of the lack of rapid formation of metal oxide. This may be attributed to the close packed structure of these metals, which would prevent diffusion of the oxygen inward, and the high cohesive energy, which would prevent movement of metal atoms outward. The lack of these properties would cause lead and aluminum to react more rapidly with oxygen to form the oxide.

Reversible adsorption on the oxidized films caused reversible potential changes, and are believed to be due to polarization of adsorbed molecules or atoms attached with the negative side out. This forms an electric double layer which would increase the effective work function of the metal. This increase would be less than in the case of an adsorbed layer of ions. Mignotet (36) studied the adsorption of nitrogen and inert gases on evaporated nickel films at liquid nitrogen temperatures and he observed relatively large potential changes due to physical adsorption. However, he reports a decrease in the work function for physical adsorption; in this work at room temperature physical adsorption always involved an increase.

In this work the decrease in work function that occurred after the initial oxygen adsorption ranged from 0.433 to 0.989 electron volts for the various metals. The differences of the final potentials of the oxidized films were about the same as the differences of the work functions of the pure metals. These comparisons are given in Table 3.

Table 3

Over-all Potential Changes of Films

Metal	Number Averaged	$\Delta\phi$, Au. Decrease*	Au. V, Final	ϕ , Intrinsic (37)
Aluminum	6	0.937 v.	1.414 v.	3.38 e.v.
Chromium	2	0.765	0.296	4.38
Nickel	1	0.811	0.278	4.32
Iron	2	0.989	0.371	4.40
Lead	1	0.433	0.833	3.94

* See context for explanation

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Nitrogen showed no permanent reaction with the metals studied. At room temperature, such a reaction would be expected to be negligibly slow. The physical adsorption of this gas caused an increase in ϕ which could be reversed, as was true for physically adsorbed oxygen.

Water vapor increased the oxidation rate of lead, but apparently did not affect the oxidation of the other metals. At higher vapor pressures, an adsorbed film of water vapor probably increases the oxidation rate through local cell reactions, as described in corrosion theory.

The oxides of iron, nickel, and chromium are known to form semi-conductors. The question arises as to whether or not the observed potential trends can be correlated with a change of semi-conductor type in the thin oxide film. There seems to be no answer to this question from contact potential data alone.

The studies with the three transition metals indicate that the transitory passive states found in electrochemical systems can be caused by an adsorbed layer of oxygen ions.

The proposed ionic mechanism suggests the possibility that heterogeneous catalysts might operate in oxidation reactions by ionizing the adsorbed oxygen to provide a source of active oxygen. This requires that the catalyst have some of the observed properties of the evaporated films, at the conditions where catalysts are used. Reactive metals such as aluminum would become inactivated too quickly to be good catalysts. On the other hand, the transition metals presumably could ionize adsorbed oxygen without rapidly forming an oxide; this state would then serve as a source of active oxygen for the reaction.

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